CLAIMS

What is claimed is:

1. A process for the polymerization of olefins, comprising the step of contacting, at a temperature of about -100°C to about $+200^{\circ}\text{C}$, one or more monomers selected from the group consisting of ethylene and an olefin of the formula $\text{H}_2\text{C=CH}(\text{CH}_2)_n\text{H}$ (XXII), and a Cr, Mn, V, Ti, Zr or Hf complex of an anion of the formula (I)

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$$\begin{bmatrix} R^2 & & \\ R^1 & & \\$$

wherein:

R¹ is hydrocarbyl or substituted hydrocarbyl,

R² is hydrogen, hydrocarbyl or substituted hydrocarbyl,

and R³ is hydrogen, hydrocarbyl, substituted

hydrocarbyl or a functional group, provided that R¹ and

R² taken together may be ortho-arylene or substituted

ortho-arylene, or R¹, R² and R³ taken together may form

one or more rings;

 $\rm Z$ is a bridging group of the formula (II), (III) or (IV)

$$R^{20}$$
 R^{6}
 R^{10}
 R^{12}
 R^{12}
 R^{13}
 R^{21}
 R^{22}
 R^{22}
 R^{22}
 R^{22}
 R^{21}
 R^{3}
 R^{14}
 R^{13}
 R^{15}
 R^{15}
 R^{15}
 R^{10}
 R^{12}
 R^{13}
 R^{13}
 R^{13}
 R^{14}
 R^{15}
 R^{15}
 R^{15}
 R^{15}
 R^{15}

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Q is nitrogen, oxygen, phosphorous or sulfur, provided that when Z is (II), Q is oxygen;

 ${\sf R}^4$ is hydrogen, hydrocarbyl or substituted hydrocarbyl, provided that when Q is oxygen or sulfur ${\sf R}^4$ is not present;

 ${\bf R}^6$ is hydrogen, hydrocarbyl or substituted hydrocarbyl, provided that ${\bf R}^3$ and ${\bf R}^6$ together may form a ring;

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 ${\bf R}^7$ is hydrogen, hydrocarbyl or substituted hydrocarbyl, provided that ${\bf R}^3$, ${\bf R}^6$ and ${\bf R}^7$ together may form an aromatic ring, or ${\bf R}^6$ and ${\bf R}^7$ taken together may form a ring;

R⁸ is hydrogen, hydrocarbyl or substituted hydrocarbyl;

R⁹ is hydrogen, hydrocarbyl or substituted hydrocarbyl, provided that R⁴ and R⁹ taken together may be part of a double bond to an imino nitrogen atom, or R⁸ and R⁹ taken together may form a carbonyl with the carbon to which they are attached, or R⁸ and R⁹ taken together may form a ring, or R⁴ and R⁹ taken together may form a ring, or R⁴, R⁸ and R⁹ taken together may form a ring, or R⁶, R⁷, R⁸ and R⁹ taken together may form an aromatic ring;

 R^{10} , R^{11} , R^{12} and R^{13} are each independently hydrogen, hydrocarbyl or substituted hydrocarbyl, provided that R^{10} , R^{11} , R^{12} and R^{13} taken together may be ortho-arylene;

 ${\rm R}^{14}$ and ${\rm R}^{15}$ are each independently hydrogen, hydrocarbyl or substituted hydrocarbyl, provided that ${\rm R}^{14}$ and ${\rm R}^{15}$ taken together may form a carbonyl with the carbon to which they are attached, or ${\rm R}^{12}$, ${\rm R}^{13}$, ${\rm R}^{14}$, and ${\rm R}^{15}$ taken together may form an o-arylene group, or ${\rm R}^{10}$, ${\rm R}^{11}$, ${\rm R}^{12}$, ${\rm R}^{13}$, ${\rm R}^{14}$, and ${\rm R}^{15}$ taken together may form a fused aromatic ring system, or ${\rm R}^{13}$ and ${\rm R}^{14}$ taken together may form a ring;

 R^{20} and R^{21} are each independently hydrogen, 35 hydrocarbyl or substituted hydrocarbyl, or R^{20} and R^{21} taken together may form a ring;

each R^{22} is individually hydrocarbyl, oxygen or alkoxy, provided that when R^{22} is oxygen, two of R^{22} are taken together to form T=O;

n is an integer of 1 or more;

T is phosphorous or sulfur whose oxidation state is 3 or greater; and

x is equal to the oxidation state of T minus 2.

- 2. The process as recited in claim 1, wherein the monomer is ethylene.
- 10 3. The process as recited in claim 1, wherein the transition metal is selected from the group consisting of Zr and Ti.
 - 4. The process as recited in claim 1, wherein R^1 and R² taken together are o-arylene, Z is a group of the formula (III), Q is oxygen, and R^6 , R^7 , R^8 and R^9 taken together form an aromatic ring.
 - 5. The process as recited in claim 4, wherein (I) has the formula

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wherein R^{24} , R^{25} , R^{26} , R^{27} , R^{29} , R^{30} , R^{31} and R^{32} are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or a functional group, and R²⁸ is hydrogen, hydrocarbyl, or substituted hydrocarbyl, provided that 25 any two of R^{24} , R^{25} , R^{26} , R^{27} , R^{29} , R^{30} , R^{31} and R^{32} vicinal to one another may be taken together to form a ring, and that R^{27} and R^{28} may be taken together to form a ring, or R^{28} and R^{29} may be taken together to form a ring.

6. A process for the polymerization of olefins, comprising the step of contacting, at a temperature of about $-100\,^{\circ}\text{C}$ to about $+200\,^{\circ}\text{C}$, one or more monomers selected from the group consisting of ethylene and $\text{H}_2\text{C=CH}(\text{CH}_2)_n\text{H}$ (XXII), with a compound of the formula (V)

$$R^{1}$$
 R^{1}
 R^{3}
 R^{4}
 R^{4}
 R^{4}
 R^{4}

10 wherein:

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 R^1 is hydrocarbyl or substituted hydrocarbyl, R^2 is hydrogen, hydrocarbyl or substituted hydrocarbyl, and R^3 is hydrogen, hydrocarbyl, substituted hydrocarbyl or a functional group, provided that R^1 and R^2 taken together may be ortho-arylene or substituted ortho-arylene, or R^1 , R^2 and R^3 taken together may form one or more rings;

 $\ensuremath{\text{Z}}$ is a bridging group of the formula (II), (III) or (IV)

 R^{20} R^{6} R^{10} R^{12} R^{12} R^{13} R^{22} R^{22} R^{22} R^{22} R^{3} R^{11} R^{13} R^{13} R^{14} R^{15} R^{15} R^{15} R^{15} R^{15}

 ${\tt Q}$ is nitrogen, oxygen, phosphorous or sulfur, provided that when Z is (II), Q is oxygen;

 ${\sf R}^4$ is hydrogen, hydrocarbyl or substituted hydrocarbyl, provided that when Q is oxygen or sulfur ${\sf R}^4$ is not present;

 ${\bf R}^6$ is hydrogen, hydrocarbyl or substituted hydrocarbyl, provided that ${\bf R}^3$ and ${\bf R}^6$ taken together may form a ring;

 ${\bf R}^7$ is hydrogen, hydrocarbyl or substituted hydrocarbyl, provided that ${\bf R}^3$, ${\bf R}^6$ and ${\bf R}^7$ taken together may form an aromatic ring, or ${\bf R}^6$ and ${\bf R}^7$ taken together may form a ring;

 ${\sf R}^{\sf 8}$ is hydrogen, hydrocarbyl or substituted hydrocarbyl;

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10 R⁹ is hydrogen, hydrocarbyl or substituted hydrocarbyl, provided that R⁴ and R⁹ taken together may be part of a double bond to an imino nitrogen atom, or R⁸ and R⁹ taken together may form a carbonyl with the carbon to which they are attached, or R⁸ and R⁹ taken together may form a ring, or R⁴ and R⁹ taken together may form a ring, or R⁴, R⁸ and R⁹ taken together may form a ring, or R⁶, R⁷, R⁸ and R⁹ taken together may form an aromatic ring;

 R^{10} , R^{11} , R^{12} and R^{13} are each independently hydrogen, hydrocarbyl or substituted hydrocarbyl, provided that R^{10} , R^{11} , R^{12} and R^{13} taken together may be ortho-arylene;

 R^{14} and R^{15} are each independently hydrogen, hydrocarbyl or substituted hydrocarbyl, provided that R^{14} and R^{15} taken together may form a carbonyl with the carbon to which they are attached, or R^{12} , R^{13} , R^{14} , and R^{15} taken together may form an o-arylene group, or R^{10} , R^{11} , R^{12} , R^{13} , R^{14} , and R^{15} taken together may form a fused aromatic ring system, or R^{13} and R^{14} taken together may form a ring;

 $\rm R^{20}$ and $\rm R^{21}$ are each independently hydrogen, hydrocarbyl or substituted hydrocarbyl, or $\rm R^{20}$ and $\rm R^{21}$ taken together may form a ring;

each R^{22} is individually hydrocarbyl, oxygen or alkoxy, provided that when R^{22} is oxygen, two of R^{22} are taken together to form T=0;

n is an integer of 1 or more;

T is phosphorous or sulfur whose oxidation state is 3 or greater;

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x is equal to the oxidation state of T minus 2; M is Ti, Zr, Hf, V, Mn or Cr;

 ${\tt m}$ is an integer equal to the valence of M minus 2; and

each L^1 is independently a monodentate monoanionic ligand and at least for one of L^1 an ethylene molecule may insert between L^1 and M, and L^2 is a monodentate neutral ligand which may be displaced by ethylene or an empty coordination site, provided that an L^1 and L^2 taken together may be a monoanionic polydentate ligand and at least for one of these monoanionic polydentate ligands ethylene may insert between said monoanionic polydentate ligand and M.

- 7. The process as recited in claim 6, wherein the monomer is ethylene.
- 8. The process as recited in claim 6, wherein the transition metal is selected from the group consisting of Zr and Ti.
- 9. The process as recited in claim 6, wherein R^1 and R^2 taken together are o-arylene, Z is a group of the formula (III), Q is oxygen, and R^6 , R^7 , R^8 and R^9 taken together form an aromatic ring.
- 10. The process as recited in claim 6, wherein (V) has the formula

$$R^{25}$$
 R^{26}
 R^{27}
 R^{28}
 R^{29}
 R^{30}
 R^{31}
 R^{32}
 R^{31}
 R^{32}
 R^{31}

30 wherein R^{24} , R^{25} , R^{26} , R^{27} , R^{29} , R^{30} , R^{31} and R^{32} are each independently hydrogen, hydrocarbyl, substituted

hydrocarbyl or a functional group, and R^{28} is hydrogen, hydrocarbyl, or substituted hydrocarbyl, provided that any two of R^{24} , R^{25} , R^{26} , R^{27} , R^{29} , R^{30} , R^{31} and R^{32} vicinal to one another may be taken together to form a ring, and that R^{27} and R^{28} may be taken together to form a ring, or R^{28} and R^{29} may be taken together to form a ring.

11. The process as recited in claim 6, wherein the monomers and compound of the formula (V) are contacted in the further presence of a catalyst activator.

12. A compound of the formula (VI)

$$R^{1}$$
 R^{2}
 R^{3}
 R^{3}
 R^{4}
 R^{4}
 R^{4}
 R^{3}

15 wherein:

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 R^1 is hydrocarbyl or substituted hydrocarbyl, R^2 is hydrogen, hydrocarbyl or substituted hydrocarbyl, and R^3 is hydrogen, hydrocarbyl, substituted hydrocarbyl or a functional group, provided that R^1 and R^2 taken together may be ortho-arylene or substituted ortho-arylene, or R^1 , R^2 and R^3 taken together may form one or more rings;

 $\rm Z$ is a bridging group of the formula (II), (III) or (IV)

$$R^{20}$$
 R^{6}
 R^{10}
 R^{12}
 R^{12}
 R^{13}
 R^{22}
 R^{22}
 R^{22}
 R^{22}
 R^{22}
 R^{21}
 R^{3}
 R^{12}
 R^{13}
 R^{13}
 R^{13}
 R^{14}
 R^{15}
 R^{15}
 R^{15}
 R^{15}

Q is nitrogen, oxygen, phosphorous or sulfur, provided that when Z is (II), Q is oxygen;

 ${\sf R}^4$ is hydrogen, hydrocarbyl or substituted hydrocarbyl, provided that when Q is oxygen or sulfur ${\sf R}^4$ is not present;

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 R^6 is hydrogen, hydrocarbyl or substituted hydrocarbyl, provided that R^3 and R^6 taken together may form a ring;

 ${\sf R}^7$ is hydrogen, hydrocarbyl or substituted 10 hydrocarbyl, provided that ${\sf R}^3$, ${\sf R}^6$ and ${\sf R}^7$ taken together may form an aromatic ring, or ${\sf R}^6$ and ${\sf R}^7$ taken together may form a ring;

 ${\sf R}^{\sf 8}$ is hydrogen, hydrocarbyl or substituted hydrocarbyl;

15 R⁹ is hydrogen, hydrocarbyl or substituted hydrocarbyl, provided that R⁴ and R⁹ taken together may be part of a double bond to an imino nitrogen atom, or R⁸ and R⁹ taken together may form a carbonyl with the carbon to which they are attached, or R⁸ and R⁹ taken together may form a ring, or R⁴ and R⁹ taken together may form a ring, or R⁴, R⁸ and R⁹ taken together may form a ring, or R⁶, R⁷, R⁸ and R⁹ taken together may form an aromatic ring;

 R^{10} , R^{11} , R^{12} and R^{13} are each independently hydrogen, hydrocarbyl or substituted hydrocarbyl, provided that R^{10} , R^{11} , R^{12} and R^{13} taken together may be ortho-arylene;

R¹⁴ and R¹⁵ are each independently hydrogen, hydrocarbyl or substituted hydrocarbyl, provided that R¹⁴ and R¹⁵ taken together may form a carbonyl with the carbon to which they are attached, or R¹², R¹³, R¹⁴, and R¹⁵ taken together may form an o-arylene group, or R¹⁰, R¹¹, R¹², R¹³, R¹⁴, and R¹⁵ taken together may form a fused aromatic ring system, or R¹³ and R¹⁴ taken together may form a ring;

 $\rm R^{20}$ and $\rm R^{21}$ are each independently hydrogen, hydrocarbyl or substituted hydrocarbyl, or $\rm R^{20}$ and $\rm R^{21}$ taken together may form a ring;

each R^{22} is individually hydrocarbyl, oxygen or alkoxy, provided that when R^{22} is oxygen, two of R^{22} are taken together to form T=O;

n is an integer of 1 or more;

T is phosphorous or sulfur whose oxidation state is 3 or greater;

x is equal to the oxidation state of T minus 2; M is Ti, Zr, Hf, V, Mn or Cr;

 $\,$ m is an integer equal to the valence of M minus 10 $\,$ 2; and

p is 0 or 1; and

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each L^3 is independently a monodentate monoanionic ligand, and L^4 is a monodentate neutral ligand or an empty coordination site, provided that an L^3 and L^4 taken together may be a monoanionic bidentate ligand.

13. The compound as recited in claim 12, wherein M is selected from the group consisting of Zr and Ti.

14. The compound as recited in claim 12, wherein R^1 and R^2 taken together are o-arylene, Z is a group of the formula (III), Q is oxygen, and R^6 , R^7 , R^8 and R^9 taken together form an aromatic ring.

15. The compound as recited in claim 12, wherein (VI) has the formula

$$R^{25}$$
 R^{24}
 R^{28}
 R^{29}
 R^{30}
 R^{31}
 R^{32}
 R^{31}
 R^{32}
 R^{31}

wherein R^{24} , R^{25} , R^{26} , R^{27} , R^{29} , R^{30} , R^{31} and R^{32} are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or a functional group, and R^{28} is hydrogen, hydrocarbyl, or substituted hydrocarbyl, provided that any two of R^{24} , R^{25} , R^{26} , R^{27} , R^{29} , R^{30} , R^{31} and R^{32}

vicinal to one another may be taken together to form a ring, and that R^{27} and R^{28} may be taken together to form a ring, or R^{28} and R^{29} may be taken together to form a ring.

5 16. A polymerization catalyst component comprising a Ti, Zr, Hf, V, Mn or Cr complex of an anion of the formula (I)

$$\begin{bmatrix} R^2 & \\ R^1 & \\ Q & \\ R^4 & \end{bmatrix} = (I)$$

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wherein:

 ${\bf R}^1$ is hydrocarbyl or substituted hydrocarbyl, ${\bf R}^2$ is hydrogen, hydrocarbyl or substituted hydrocarbyl, and ${\bf R}^3$ is hydrogen, hydrocarbyl, substituted

hydrocarbyl or a functional group, provided that R^1 and R^2 taken together may be ortho-arylene or substituted ortho-arylene, or R^1 , R^2 and R^3 taken together may form one or more rings;

 $$\rm Z$$ is a bridging group of the formula (II), 20 (III) or (IV)

$$R^{20}$$
 R^{6}
 R^{8}
 R^{11}
 R^{12}
 R^{13}
 R^{22}
 R^{22}
 R^{22}
 R^{22}
 R^{22}
 R^{21}
 R^{22}
 R^{3}
 R^{14}
 R^{13}
 R^{15}
 R^{15}
 R^{15}
 R^{10}
 R^{12}
 R^{13}
 R^{13}
 R^{14}
 R^{15}
 R^{15}
 R^{15}
 R^{15}

Q is nitrogen, oxygen, phosphorous or sulfur, 25 provided that when Z is (II), Q is oxygen;

 ${\sf R}^4$ is hydrogen, hydrocarbyl or substituted hydrocarbyl, provided that when Q is oxygen or sulfur ${\sf R}^4$ is not present;

 ${\bf R}^6$ is hydrogen, hydrocarbyl or substituted hydrocarbyl, provided that ${\bf R}^3$ and ${\bf R}^6$ together may form a ring;

 ${\bf R}^7$ is hydrogen, hydrocarbyl or substituted hydrocarbyl, provided that ${\bf R}^3$, ${\bf R}^6$ and ${\bf R}^7$ together may form an aromatic ring, or ${\bf R}^6$ and ${\bf R}^7$ taken together may form a ring;

 ${\sf R}^{\sf 8}$ is hydrogen, hydrocarbyl or substituted hydrocarbyl;

10 R⁹ is hydrogen, hydrocarbyl or substituted hydrocarbyl, provided that R⁴ and R⁹ taken together may be part of a double bond to an imino nitrogen atom, or R⁸ and R⁹ taken together may form a carbonyl with the carbon to which they are attached, or R⁸ and R⁹ taken together may form a ring, or R⁴ and R⁹ taken together may form a ring, or R⁴, R⁸ and R⁹ taken together may form a ring, or R⁶, R⁷, R⁸ and R⁹ taken together may form an aromatic ring;

 R^{10} , R^{11} , R^{12} and R^{13} are each independently hydrogen, hydrocarbyl or substituted hydrocarbyl, provided that R^{10} , R^{11} , R^{12} and R^{13} taken together may be ortho-arylene;

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 R^{14} and R^{15} are each independently hydrogen, hydrocarbyl or substituted hydrocarbyl, provided that R^{14} and R^{15} taken together may form a carbonyl with the carbon to which they are attached, or R^{12} , R^{13} , R^{14} , and R^{15} taken together may form an o-arylene group, or R^{10} , R^{11} , R^{12} , R^{13} , R^{14} , and R^{15} taken together may form a fused aromatic ring system, or R^{13} and R^{14} taken together may form a ring;

 $\rm R^{20}$ and $\rm R^{21}$ are each independently hydrogen, hydrocarbyl or substituted hydrocarbyl, or $\rm R^{20}$ and $\rm R^{21}$ taken together may form a ring;

each R^{22} is individually hydrocarbyl, oxygen or alkoxy, provided that when R^{22} is oxygen, two of R^{22} are taken together to form T=O;

n is an integer of 1 or more;

T is phosphorous or sulfur whose oxidation state is 3 or greater; and

x is equal to the oxidation state of T minus 2.

- 17. The polymerization catalyst component as recited in claim 16, wherein the transition metal is selected from the group consisting of Zr and Ti.
- 18. The polymerization catalyst component as recited in claim 16, wherein R^1 and R^2 taken together are o-arylene, Z is a group of the formula (III), Q is oxygen, and R^6 , R^7 , R^8 and R^9 taken together form an aromatic ring.
- 19. The polymerization catalyst component as recited in claim 18, wherein (I) has the formula

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wherein R^{24} , R^{25} , R^{26} , R^{27} , R^{29} , R^{30} , R^{31} and R^{32} are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or a functional group, and R^{28} is hydrogen, hydrocarbyl, or substituted hydrocarbyl, provided that any two of R^{24} , R^{25} , R^{26} , R^{27} , R^{29} , R^{30} , R^{31} and R^{32} vicinal to one another may be taken together to form a ring, and that R^{27} and R^{28} may be taken together to form a ring, or R^{28} and R^{29} may be taken together to form a ring.

20. The polymerization catalyst component as recited in claim 16, further comprising a catalyst activator.